Interactions of Chlorpyrifos with Colloidal Materials in Aqueous Systems

Jigang Wu and David A. Laird*

ABSTRACT

An understanding of sorptive processes is key to describing the fate of chlorpyrifos [O,O-diethyl-O-(3, 5, 6-trichloro-2-pyridyl) phosphorothioate] in aquatic environments. The objectives of this study were to evaluate isotherms for adsorption and desorption of chlorpyrifos on colloidal materials and to advance understanding of interaction mechanisms between chlorpyrifos and colloidal materials. Six Ca-saturated reference smectites, one Ca-saturated humic acid (Ca-humate), and one suspended sediment sample, collected from the Upper Cedar River, Iowa, were studied. A batch equilibration technique was employed to quantify adsorption and desorption isotherms for chlorpyrifos over the 0 to 100 μg L^{-1} concentration range in a 0.01 M CaCl$_2$ background. Large differences in sorption affinity and variation in desorption hysteresis were found among the smectites. Neither chlorpyrifos adsorption nor its desorption were correlated with cation exchange capacity, surface area, or surface charge density of the smectites. The evidence suggests that physical interaction between chlorpyrifos and smectites is the dominant mechanism for adsorption of chlorpyrifos in aqueous systems. Chlorpyrifos was very strongly sorbed on Ca-humate and was not desorbed from the Ca-humate back into the aqueous solution. Chlorpyrifos was moderately sorbed on river sediment, and a large adsorption–desorption hysteresis was also found. The study implies that the nature of both organic and inorganic materials in suspended sediment can influence the adsorption–desorption behavior of chlorpyrifos in aqueous systems.

CHLORPYRIFOS, the active ingredient in Dursban and Lorsban (Dow AgroSciences, Indianapolis, IN), has been used for many years in agriculture for the control of various crop insect pests (Racke, 1993). It is estimated that more than 3 million kg of chlorpyrifos are applied to field crops in the United States annually (USDA Economic Research Service, 1994). Chlorpyrifos bound to soil constituents may be introduced into rivers by surface runoff from agricultural lands, and recent work indicates that chlorpyrifos bound to suspended colloids is toxic to aquatic organisms (Phillips et al., 2003).

Kratzer (1998) reported a considerable increase in the concentrations of suspended solids, organic compounds, pesticides, metals, and other contaminants that may be toxic to biota in surface waters as a result of surface runoff from storm events. While silt- and sand-size particles may represent a significant fraction of the mass of suspended sediment, the vast majority of reactive surfaces are associated with suspended colloids. In rivers, suspended colloidal materials are made up predominantly of clay minerals and organic matter, the same constituents responsible for retention of pesticides in soils (Koskinen and Harper, 1990). Understanding the interaction between chlorpyrifos and colloidal materials in aqueous systems is fundamental for assessing fate and potential toxicity of chlorpyrifos bound to suspended sediment in aquatic environments.

The sorption of chlorpyrifos on soils and sediments has been investigated by a number of researchers (Felsot and Dahm, 1979; Sharom et al., 1980; Macalady and Wolfe, 1985). The moderately high partition coefficients that have been determined for chlorpyrifos result from its nonpolar nature and indicate its tendency to associate strongly with organic materials in the environment. Racke (1993) comprehensively reviewed adsorption coefficients that have been determined in the laboratory using the batch equilibrium method. For chlorpyrifos, sorption K_d values ranged from 13.4 to 1862.0.

Laird et al. (1992) investigated the effects of surface charge density on sorption of atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) by Ca-smectites. They found that from 0 to 100% of added atrazine was adsorbed on the Ca-smectites from 0.01 M CaCl$_2$ aqueous systems, and the affinity of smectites for atrazine increased with decreasing surface charge density of reference smectites. They concluded that smectite surface chemistry strongly influences atrazine sorption. Chlorpyrifos is dominantly a nonpolar compound, while atrazine has both polar and nonpolar moieties. Therefore, it is not known whether chlorpyrifos sorption on smectites will exhibit a similar relationship.

The objectives of this study were to (i) evaluate isotherms for adsorption and desorption of chlorpyrifos on colloidal materials in aqueous systems, (ii) evaluate the relationship between chlorpyrifos sorptive behavior and surface properties of smectites, and (iii) advance understanding of the mechanism for interactions between chlorpyrifos and colloidal materials in aqueous systems. The significance of this study lies in the prediction of the fate and toxicity of chlorpyrifos associated with suspended sediment in aquatic environments.

MATERIALS AND METHODS

Reagent-grade chlorpyrifos with purity of 99.2% was obtained from Chem Service (West Chester, PA). The structure of chlorpyrifos is shown in Fig. 1. Ethanol (100%) was used to help dissolve chlorpyrifos for preparation of stock solutions. All solutions and suspensions were prepared using Milli-Q water with a resistivity of 18.2 MΩ-cm (Milli-Q Plus system; Millipore, Billerica, MA).

J. Wu, Department of Agronomy, Iowa State University, Ames, IA 50011. Current address: Institute of Mountain Hazards and Environment, Chinese Academy of Sciences, Chengdu, Sichuan 610041 China. David A. Laird, National Soil Tilth Laboratory, USDA-ARS, Ames, IA 50011. Received 12 Nov. 2003. *Corresponding author (laird@nstl.gov).

Abbreviations: GC, gas chromatography; K_d, distribution coefficient; $K_{d,ad}$, adsorption distribution coefficient; $K_{d,de}$, desorption distribution coefficient; SPME, solid-phase microextraction.
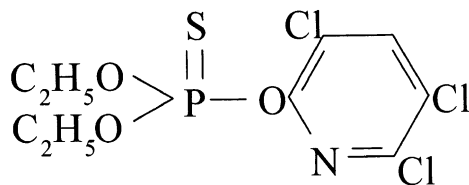
$$C_2H_5O$$

Fig. 1. Chemical structure of chlorpyrifos.

Sample Preparation

Six reference smectites [Amory montmorillonite (Amory), Polkville montmorillonite (Polkville), Panther Creek beidellite (Panther), Otay white montmorillonite (Otay), IMV saponite (Saponite), Floridin hectorite (Hectorite)] were evaluated in this study. Amory and Polkville were obtained from the Ward's Natural Science Establishment (Rochester, NY). Panther was acquired from the A.D. Scott collection (Iowa State University, Ames, IA). Otay was collected at an exposure near San Diego, CA. Saponite and Hectorite were obtained from IMV Corporation, a division of Floridin Company (Amargosa Valley, NV). Carbonates in smectites were removed by treatment with pH 5.0, 1.0 M NaC$_2$H$_3$O$_2$ (Kunze and Dixon, 1986). The clay fraction (<2 μm) was separated by sedimentation from the bulk ore. The clays were Ca-saturated by treatment with 1 M CaCl$_2$. The Ca-saturated clays were dialyzed using Spectra/Por 3500 MWCO molecularporous membrane tubing against Milli-Q water until the conductivity of the dialysate was <0.2 mS m^{-1}. The Ca-saturated samples were then freeze-dried.

Humic acid was obtained from Aldrich Chemical Company (Milwaukee, WI). The humic acid was washed with 1.0 M CaCl$_2$ four times to prepare Ca-saturated humic acid (Ca-humate), dialyzed using Spectra/Por 3500 MWCO molecularporous membrane tubing against Milli-Q water until no Cl$^-$ was detected by AgNO$_3$, and then freeze-dried.

A large volume of river water (approximately 950 L) containing suspended sediment was collected from the Upper Cedar River near Janesville, IA. The suspended sediment was separated from the river water by freezing-induced flocculation, thawing, and sedimentation. The concentrated suspended sediment sample was then freeze-dried.

No chemical treatments were used to prepare the dried sediment sample.

Characterization of Samples

The total elemental composition and structural chemistry of reference smectites were previously reported by Laird et al. (1992). The clay mineralogy of the smectites and the sediment sample was analyzed by X-ray diffraction (XRD) using oriented specimens on glass slides and CuKα radiation with a Siemens (Munich, Germany) D5000 X-ray diffractometer (Moore and Reynolds, 1989). Total C and N of the smectite and sediment samples were determined by thermal combustion of untreated samples using a Carlo Erba NA 1500 NSC elemental analyzer (Haake Buchler Instruments, Paterson, NJ). Organic C in the smectites was determined by thermal combustion analysis of samples that had been pretreated with 1:3 HCl to remove trace carbonate. Inorganic C in the smectites was determined by thermal combustion analysis of samples that had been pretreated with 30% H$_2$O$_2$ to oxidize trace organic C. Inorganic C of the sediment was determined by a titrimetric method (Bundy and Bremner, 1972). Organic C in the sediment was determined by the difference between total C and inorganic C. The particle-size analysis of the sediment sample was performed using the pipet method (Gee and Bauder, 1986).

Sorption and Desorption of Chlorpyrifos

Chlorpyrifos adsorption and desorption isotherms were obtained using the batch equilibration procedure. Triplicate 0.2-g samples of clay, sediment, or Ca-humate were equilibrated with 20 mL of 0.01 M CaCl$_2$ solution [adjusted to pH 6.0 with HCl or Ca(OH)$_2$] containing 0 to 100 μg L^{-1} of chlorpyrifos in 25-mL Corex glass centrifuge tubes by shaking for 24 h at room temperature (23 $\pm$ 2°C). The solutions contained a small amount of ethanol (<0.25% by volume), which was added with the chlorpyrifos. Aqueous and solid phases were separated by centrifugation (17 210 × g) for 30 min. Supernatant (10 mL) was withdrawn to quantify chlorpyrifos in the aqueous phase. The amount of chlorpyrifos sorbed on the samples was calculated from the difference between the initial and equilibrium solution concentrations.

Desorption of chlorpyrifos was performed using the samples initially equilibrated with 100 μg L^{-1} of chlorpyrifos by first adding 10 mL of fresh 0.01 M CaCl$_2$ to replace that which had been removed and then shaking the samples for 24 h at 23 $\pm$ 2°C. Aqueous and solid phases were separated by centrifugation as described above. The desorption procedure was repeated five times for each sample.

Solid-Phase Microextraction–Gas Chromatography Analysis

Chlorpyrifos in aqueous samples was quantified using a solid-phase microextraction (SPME)–gas chromatography (GC) technique developed in our laboratory. The SPME device was obtained from Supelco (Bellefonte, PA). The SPME fiber, coated with 85-μm polyacrylate, was used for the determination of chlorpyrifos after evaluation of a variety of available fibers.

A 10-mL aqueous sample was pipetted into an amber glass vial. The SPME fiber was completely immersed into the solution, which was stirred at a constant rate during a 30-min equilibration. The SPME fiber was then inserted directly into the gas chromatograph injector port for desorption and analysis of chlorpyrifos. Under these conditions, intensity of the chlorpyrifos peak was proportional to the chlorpyrifos concentration in the aqueous sample.

All analyses were performed using a Hewlett-Packard (Palo Alto, CA) 5890 Series II gas chromatograph equipped with a flame ionization detector. A split/splitless GC injection port, maintained at 220°C, and a 30-m × 0.25-mm-i.d. DB-1701 fused silica capillary column with a 0.25-μm stationary film (J&W Scientific, Folsom, CA) were used. The GC oven's initial temperature was 50°C, and it was ramped to a final temperature of 260°C at 5°C min^{-1}. The final temperature was held for 10 min. Analyte desorption from the fiber and purge off time were 5 min. The carrier gas was He with the head pressure set to 69 KPa (10 psi). The detector temperature was maintained at 260°C. The retention time of chlorpyrifos was 43.2 min based on analysis of calibration standards. A linear calibration with a coefficient of determination (r^2) greater than 0.9995 was achieved for chlorpyrifos over the concentration range of the study (0 to approximately 1000 μg L^{-1}). The limit of detention for chlorpyrifos in water using the SPME–GC method was about 0.1 μg L^{-1} and was determined by successive dilution of chlorpyrifos solutions until no distinct peak in the chromatographs was detected.

Data Analyses

The sorption distribution coefficient (K_d) of chlorpyrifos is defined by the following equation:
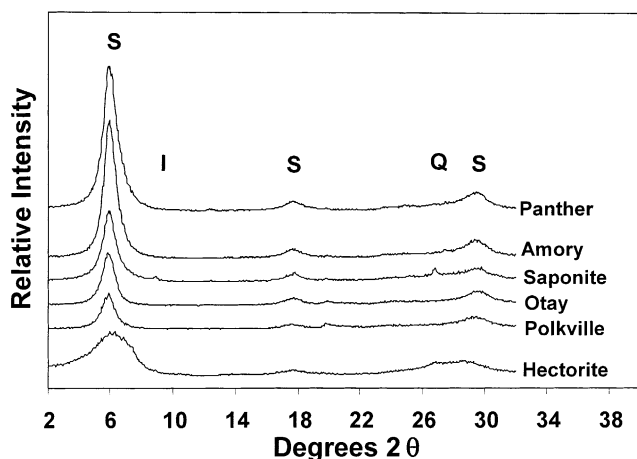
Fig. 2. X-ray diffraction patterns of Ca-saturated reference smectites equilibrated at 54% relative humidity (S, smectite; I, illite; Q, quartz).

$$K_d = C_s/C_{aq}$$

where C_s is the amount of chlorpyrifos sorbed on smectite (mg kg^{-1}) and C_{aq} is the amount of chlorpyrifos in solution (mg L^{-1}). Linear regression analysis was performed to find the correlation between K_d and surface properties of Ca-smectites. All data points or standard errors of triplicate treatments are shown in adsorption and desorption isotherms.

RESULTS AND DISCUSSION

Characterization of Smectites and Suspended Sediment

X-ray diffraction analysis indicated that smectite was the dominant mineral phase in all of the clay samples used in the study (Fig. 2). The Saponite sample was dominated by smectite, but contained lesser amounts of illite and quartz. Among the smectites, Hectorite and Saponite are trioctahedral smectites and the others are dioctahedral smectites. Table 1 presents surface properties of the smectites and indicates a large range of surface charge density among samples. Total, organic, and inorganic C contents of the studied smectites are reported in Table 2. Only trace amounts of C were found in Otay, Polkville, Amory, and Saponite, while slightly higher C contents were found for the Hectorite and Panther samples. About half of the residual C was carbonate, due apparently to incomplete removal of carbonate by the 1.0 M NaC$_2$H$_3$O$_2$ buffer (pH 5.0) treatment during sample preparation.

The suspended sediment sample contained 105.7 g kg^{-1} total C (including 18.4 g kg^{-1} organic C and 87.3 g kg^{-1}

Table 1. Surface properties of selected reference smectites. Data originally presented by Laird et al. (1992).

Smectite	Cation exchange capacity	Surface area	Surface charge density
	cmol$_c$ kg^{-1}	m^2 g^{-1}	µmol$_c$ m^{-2}
Hectorite	102	743	1.38
Panther	88	619	1.42
Saponite	106	588	1.80
Amory	93	644	1.44
Polkville	111	742	1.50
Otay	134	724	1.85

Table 2. Carbon content of reference smectite samples.

Smectite	Total C	Organic C	Inorganic C
		g kg^{-1}	
Hectorite	1.5	0.9	0.8
Panther	1.1	0.8	0.3
Saponite	0.7	0.4	0.4
Amory	0.6	0.5	0.3
Polkville	0.4	0.4	0.3
Otay	0.4	0.3	0.2

inorganic C) and 2.8 g kg^{-1} total N. The particle size analysis indicated that the suspended sediment consisted of 1% sand (>0.05 mm), 73% silt (0.002–0.05 mm), and 26% clay (<0.002 mm). The sediment contained a substantial amount of calcite in sand and silt fractions, whereas the clay fraction was dominated by smectite with lesser amounts of illite, kaolinite, quartz, and calcite (Fig. 3).

Degradation of Chlorpyrifos

There is little evidence of microbial degradation of chlorpyrifos (Racke, 1993); however, the phosphorthioate ester bond is readily hydrolyzed in aqueous systems. Under acidic conditions there is little effect of pH on the rate of hydrolysis; however, the rate of hydrolysis increases rapidly under basic conditions (Chapman and Cole, 1982; Macalady and Wolfe, 1985) and increases about 3.5-fold for each 10°C rise in temperature (Meikle and Youngson, 1978). Dissolved Cu in solutions has been found to catalyze the hydrolysis of chlorpyrifos,
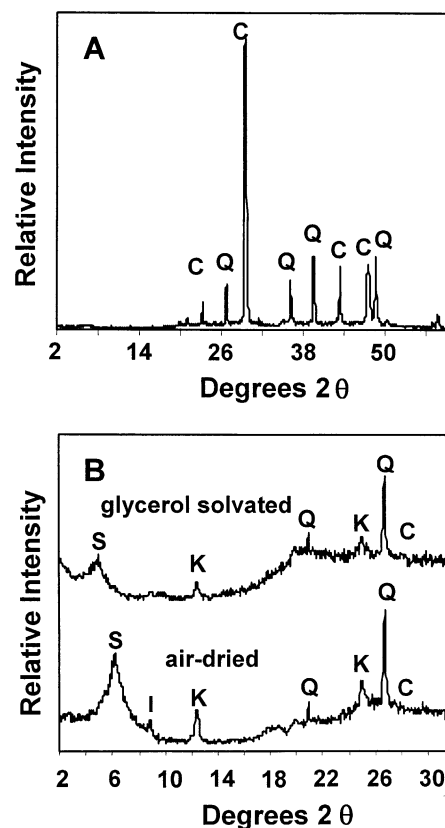

Fig. 3. X-ray diffraction patterns of suspended sediment. (A) Whole sediment. (B) Clay fraction (<2 µm) of sediment. C, calcite; I, illite; K, kaolinite; Q, quartz; S, smectite.
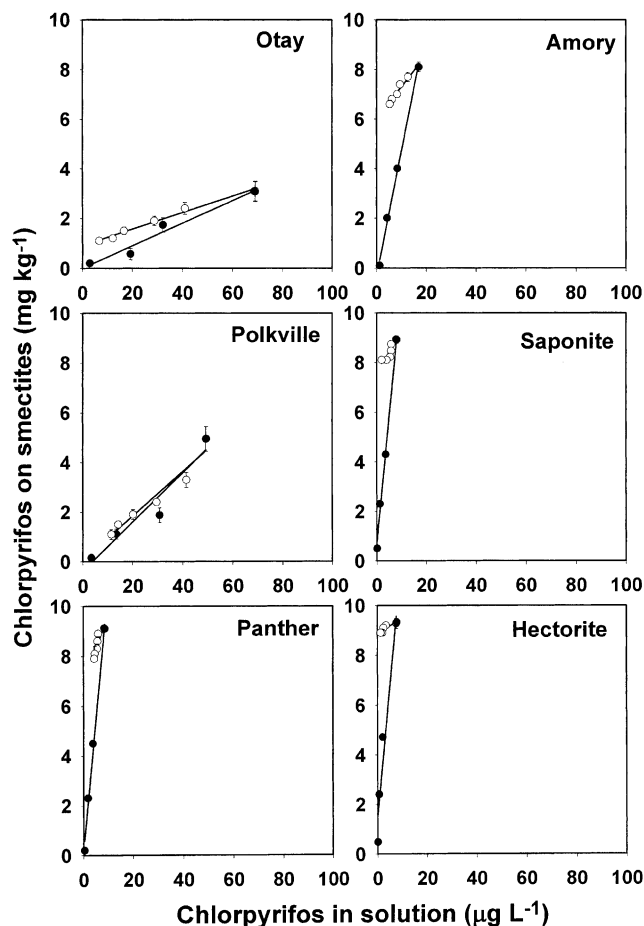
Fig. 4. Isotherms for adsorption (●) and desorption (○) of chlorpyrifos on smectites.

Fig. 5. Isotherms for adsorption and desorption of chlorpyrifos on Ca-humate (HA) and sediment.

but Ca has little effect (Mortland and Raman, 1967). We investigated the degradation kinetics of chlorpyrifos in the same aqueous and colloidal systems used in the present study (Wu and Laird, 2002). Half-lives for degradation of chlorpyrifos ranged from 27.5 to 157.5 d in aqueous systems and from 27.6 to 126.0 d in dilute colloidal systems. These results are based on 120-d incubations. By contrast, very little degradation of chlorpyrifos was observed in concentrated colloidal systems, where most of the chlorpyrifos was adsorbed, during 30-d incubations. A key conclusion of the study was that adsorption of chlorpyrifos on Ca-smectites and Ca-humate stabilizes the chlorpyrifos (inhibits hydrolysis). The results of the previous study (Wu and Laird, 2002) may be viewed as a control for the present study, and indicate that negligible hydrolysis of chlorpyrifos occurred during the 24-h equilibrations used in the present study.

Sorption and Desorption Isotherms

The adsorption isotherms (Fig. 4) indicate a large variability in sorptive behavior of chlorpyrifos in different smectite–water systems. More chlorpyrifos tended to be adsorbed on Hectorite, Saponite, and Panther while Otay and Polkville had relatively less affinity for chlorpyrifos. The results demonstrate that sorption be-
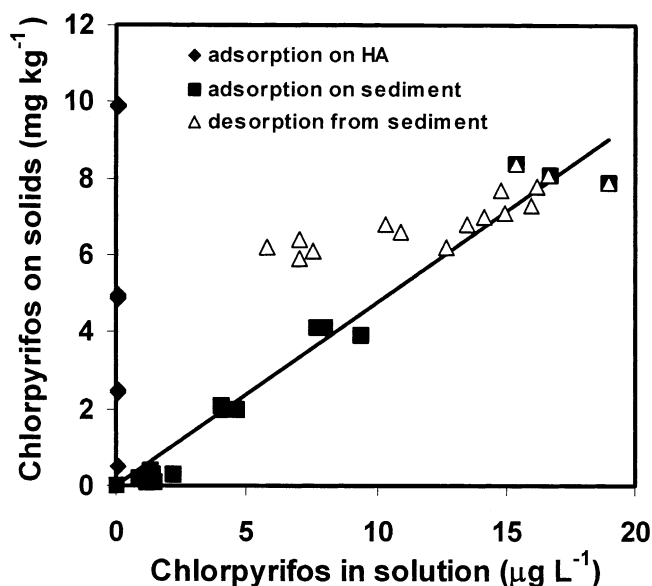
havior differs substantially, even though the selected samples are all Ca-saturated smectitic clays. The desorption isotherms show a large adsorption–desorption hysteresis among smectites that have a high affinity for chlorpyrifos, and less hysteresis for smectites with less affinity for chlorpyrifos. The desorption results show that chlorpyrifos can be weakly to moderately desorbed from smectites in aqueous solutions. By contrast, chlorpyrifos was virtually 100% sorbed on the Ca-humate and none of the sorbed chlorpyrifos was desorbed back into the aqueous solution (Fig. 5), indicating that chlorpyrifos has a strong tendency to be sorbed from water by organic materials probably due to its nonpolar nature. This strong tendency is consistent with its high octanol–water partition coefficient ($K_{ow} = 50\,000$) reported in the literature (Racke, 1993).

The Cedar River suspended sediment contained various mineral and organic materials. Figure 5 shows that the affinity of chlorpyrifos for the suspended sediment is between that of the reference smectites and the Ca-humate. Some of the chlorpyrifos sorbed on sediment was desorbed in the aqueous solution. Thus the sorptive behavior of chlorpyrifos on the suspended sediment was more like that observed for the smectites than for the Ca-humate.

Sorption Affinity and Mechanism

The adsorption affinity of smectites for chlorpyrifos can be quantified using K_d values. The K_d values for the different smectites, ranged from 45 for Otay to 1315 for Hectorite, indicate a large variation in chlorpyrifos adsorption affinity (Table 3). After five cycles of desorption, the amount of chlorpyrifos desorbed from the smectites varied from as low as 5% of the initially sorbed chlorpyrifos on the Hectorite up to 78% for Polkville. The K_d values from the desorption isotherms ($K_{d,de}$) were generally greater than those from the adsorption iso-

Table 3. Distribution coefficients (K_d) for adsorption and desorption of chlorpyrifos on selected smectites.

Smectite	$K_{d,ad}$†	$K_{d,de}$‡	Desorbed§	Total desorbed
	——— L kg^{-1} ———		mg kg^{-1}	%
Hectorite	1315 (31)	1224–6846	0.50	5.2
Panther	1069 (22)	1046–1796	1.15	12.7
Saponite	1132 (26)	1099–2857	0.92	10.1
Amory	473 (18)	476–1245	1.46	18.1
Polkville	89 (11)	80–105	3.87	78.0
Otay	45 (7)	45–162	1.98	64.5

† Average of $K_{d,ad}$ values from adsorption isotherms (standard errors are shown in parentheses).
‡ Range of $K_{d,de}$ values calculated from desorption isotherms.
§ Total amount desorbed after five repeated equilibrations.

Table 4. Correlation between adsorption ($K_{d,ad}$) and surface properties of Ca-smectites.

Property	Coefficient of determination (r^2)
Cation exchange capacity (cmol$_c$ kg^{-1})	0.37
Surface area (m^{-2} g^{-1})	0.19
Surface charge density (μmol$_c$ m^{-2})	0.10
Organic carbon (g kg^{-1})	0.57

therms ($K_{d,ad}$). The $K_{d,de}$ values increased with each desorption cycle. The difference between $K_{d,de}$ and $K_{d,ad}$ indicates the magnitude of the adsorption–desorption hysteresis.

Relationships between sorption K_d values and properties of the smectites were analyzed by regression (Table 4). The regression analysis demonstrated a weak relationship ($r^2 = 0.57$) between the K_d values and organic C content of the smectite samples, suggesting that organic C may account for some but not all of the variation in sorption affinity for the smectites. The K_d values were not significantly correlated with cation exchange capacity, surface area, or surface charge density of the smectites, suggesting that sorption affinity for chlorpyrifos is not related to surface properties of smectites. This contrasts with the observation (Laird et al., 1992) that the affinity of Ca-smectites for atrazine decreases with increasing surface charge density. Atrazine has both polar and nonpolar moieties and is therefore capable of simultaneously interacting with hydrophobic nanosites between charge sites on smectite surfaces and forming hydrogen bonds with water molecules solvating the exchangeable interlayer cations (Laird and Sawhney, 2002). Chlorpyrifos, by contrast, does not have a polar moiety that is capable of forming hydrogen bonds with water molecules. As a result, replacing the water molecules at a mineral surface with nonpolar chlorpyrifos is unfavorable from an energetic point of view. On the other hand, the adsorption of chlorpyrifos by humic materials does not require displacement of tightly bound water molecules. Although humic materials have many polar functional groups that interact strongly with water, they also have highly nonpolar regions or microsites (Stevenson, 1994). These hydrophobic microsites offer an energetically favorable environment into which a nonpolar compound may partition.

Hundal et al. (2001) investigated sorption of phenanthrene, a very nonpolar compound, by the smectites. They found a wide variation in phenanthrene sorption on smectites and a lack of correlation between sorption affinity and surface properties of the smectites. Using transmission electron microscopy they demonstrated a qualitative relationship between the general appearance or fabric of the smectites and phenanthrene sorption affinity and argued that phenanthrene was primarily retained by physical sorption. A process similar to capillary condensation, where the organic phase condenses out of the aqueous phase into a network of nano- and micropores in the smectite, was proposed to explain the observations. Results for the present study are generally consistent with the findings of Hundal et al. (2001) and suggest that physical sorption is an important mechanism for retention of chlorpyrifos by smectites in aqueous systems.

The suspended sediment sample was composed of both organic and inorganic materials. Given the extremely high affinity of Ca-humate for chlorpyrifos (Fig. 5), one might anticipate that the organic material in the suspended sediment (organic C = 18 g kg^{-1}) would dominate sorption. However, this does not appear to be the case. The adsorption–desorption isotherms for the suspended sediment resemble that of Amory more than that of the Ca-humate. The results indicate that either the organic material in the suspended sediment has substantially different properties from the studied Ca-humate or that the inorganic materials in the suspended sediment played a substantial role in retention of chlorpyrifos. The findings are significant in understanding the potential of sediments to retain and slowly release chlorpyrifos in aqueous systems and should be accounted for when modeling the fate of chlorpyrifos in aquatic environments.

CONCLUSIONS

The present study reveals a large difference in sorption affinity for chlorpyrifos and variation in adsorption–desorption hysteresis among Ca-smectites. Neither chlorpyrifos adsorption nor desorption was correlated with cation exchange capacity, surface area, or surface charge density of the smectites, suggesting that physical properties of the smectite rather than surface chemistry control chlorpyrifos sorptive behavior in aqueous systems. Capillary condensation of chlorpyrifos into a network of nano- and micropores created by smectitic quasicrystals is suggested as a possible mechanism for retention of chlorpyrifos by smectites in aqueous systems. Chlorpyrifos was very strongly sorbed on Ca-humate and was not desorbed from it into the aqueous solution. The results suggest that little chlorpyrifos sorbed on humic materials in suspended sediment would be released to aquatic environments while some chlorpyrifos sorbed on suspended clay minerals may be released to the aqueous systems depending on properties of the clays. Surprisingly, the adsorption–desorption behavior of chlorpyrifos on a suspended sediment sample more closely resembled the interaction between chlorpyrifos and Ca-smectites than between chlorpyrifos and Ca-humate. Thus the results suggest that variability in the nature of both the organic and inorganic colloidal materials in

suspended sediment may have a large influence on the adsorption–desorption behavior of chlorpyrifos.

REFERENCES

Bundy, L.G., and J.M. Bremner. 1972. A simple titrimetric method for determination of inorganic carbon in soils. Soil Sci. Soc. Am. Proc. 36:273–275.

Chapman, R.A., and C.M. Cole. 1982. Observations on the influence of water and soil pH on the persistence of insecticides. J. Environ. Sci. Health Part B B15:39–46.

Felsot, A., and P.A. Dahm. 1979. Sorption of organophosphorus and carbamate insecticides by soil. J. Agric. Food Chem. 27:557–563.

Gee, G.W., and J.W. Bauder. 1986. Particle-size analysis. p. 383–409. In A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Hundal, L.S., M.L. Thompson, D.A. Laird, and A.M. Carmo. 2001. Sorption of phenanthrene by reference smectites. Environ. Sci. Technol. 35:3456–3461.

Koskinen, W.C., and S.S. Harper. 1990. The retention process: Mechanisms. p. 51–73. In H.H. Cheng (ed.) Pesticides in the environment: Processes, impacts, and modeling. SSSA Book Ser. 2. SSSA, Madison, WI.

Kratzer, C.R. 1998. Pesticide in storm runoff from agricultural and urban areas in the Tuolumne River basin in the vicinity of Modesto, California. Water-Resour. Investigation Rep. 98-4017. USGS, Sacramento, CA.

Kunze, G.W., and J.B. Dixon. 1986. Pretreatment for mineralogical analysis. p. 91–99. In A. Klute (ed.) Methods of soil analysis. Part 1. 2nd ed. Agron. Monogr. 9. ASA and SSSA, Madison, WI.

Laird, D.A., E. Barriuso, R.H. Dowdy, and W.C. Koskinen. 1992. Adsorption of atrazine on smectites. Soil Sci. Soc. Am. J. 56:62–67.

Laird, D.A., and B.L. Sawhney. 2002. Reactions of pesticides with soil minerals. p. 765–793. In J.B. Dixon and D. Schulze (ed.) Soil mineralogy with environmental applications. SSSA Book Ser. 7. SSSA, Madison, WI.

Macalady, D.L., and N.L. Wolfe. 1985. Effects of sediment sorption and abiotic hydrolysis. 1. Organophosphorothioate esters. J. Agric. Food Chem. 33:167–173.

Meikle, R.W., and C.R. Youngson. 1978. The hydrolysis rate of chlorpyrifos, o-o-diethyl-o-(3,5,6-trichloro-2-pyridyl) phosphorothioate, and its dimethyl analog, chlorpyrifos-methyl, in dilute aqueous solution. Arch. Environ. Contam. Toxicol. 7:13–22.

Moore, D.M., and R.C. Reynolds. 1989. X-ray diffraction and the identification and analysis of clay minerals. Oxford Univ. Press, New York.

Mortland, M.M., and K.V. Raman. 1967. Catalytic hydrolysis of some organic phosphate pesticides by copper (II). J. Agric. Food Chem. 15:163–167.

Phillips, T.A., R.C. Summerfelt, J. Wu, and D.A. Laird. 2003. Toxicity of chlorpyrifos adsorbed on humic colloids to larval walleye (*Stizostedion vitreum*). Arch. Environ. Contam. Toxicol. 45:258–263.

Racke, K.D. 1993. Environmental fate of chlorpyrifos. Rev. Environ. Contam. Toxicol. 131:1–154.

Sharom, M.S., J.R.W. Miles, C.R. Harris, and F.L. McEwen. 1980. Persistence of 12 insecticides in water. Water Res. 14:1089–1093.

Stevenson, F.J. 1994. Humus chemistry: Genesis, composition, reaction. John Wiley & Sons, New York.

USDA Economic Research Service. 1994. Agricultural resources and environmental indicators. Agric. Handbook 705. USDA, Washington, DC.

Wu, J., and D.A. Laird. 2002. Hydrolysis of chlorpyrifos in aqueous and colloidal systems. Isr. J. Chem. 42:99–107.